

Claim 29. (Amended) The complex porous structure of claim 28, comprising draining following the rinsing subsequent to the oxidizing pre-treatment of the base structure.

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Claim 30. (Amended) The complex porous structure of claim 29, comprising repeating said steps following the rinsing subsequent to the oxidizing pre-treatment of the base structure a preselected number of times.

REMARKS

Minor corrections have been made to the specification, and claims 14, 18, 22, 25 and 27-30 have been amended. Claims 14-32 remain in the application. Reexamination and reconsideration of the application, as amended, are requested.

Claims 14-32 were rejected under 35 U.S.C. 112, second paragraph, as being indefinite. Claims 14, 18, 22, 25 and 27-30 have been amended to overcome these rejections. In claim 14, the basis for the addition of "throughout its entire thickness, over all its developed surface" is found at page 1, line 33-34 of the description; and the basis for the addition of "on the surface of the fibers or the opening of the structure" is found at page 6, line 10-11 of the description. In claims 29-30, the basis for the addition of "oxidising pre-treatment of the base structure" is found at page 6, line 8 of the description.

Claims 14-32 were further rejected under 35 U.S.C. 102(b) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over W094/25967 - its equivalent being U.S. Patent No. 5,683,744 to Jolly et al - JP 06248491, or DE 4023619. Claim 14 has been amended to overcome these rejections. Formal basis for the amendments to claim 14 is found in claim 14

as filed; page 1, line 17-18 (definition of foam) of the description; and page 8, line 1-3 (with a solution containing permanganate/manganate salts and/or cerium IV compounds) of the description.

amp The WO94/25967 reference teaches a method of producing of porous material layer and to the product obtained by this method. According to the Examiner, it comprises the steps of oxidising the porous polyester fabric with a solution of an oxidant and depositing a uniform polyporole coating. Jolly also discloses copper or nickel can be electrochemically deposited on the conductive textile.

The present invention differs from the Jolly reference:

- by starting from a foam defined as a base structure comprising pores, consisting of a reticulated cellular structure of high porosity greater than 80%..
- by using a solution containing the permanganate/manganate salts and/or cerium IV compounds in the oxidising step,
- by using a step-by-step process with sequential steps, and not a simultaneous oxidizing, depositing, doping step, see page column 2, line 30-35
- by the rinsing step subsequent to the oxidizing step.

Jolly et al. never refers to the use of a foam but only considers textile or paper (examples 1-24). In the present application, example 1, the foam is a 100ppI grade structure which

represents an extreme tortuosity with a low pore dimension (page 5, line 10-15 of the present specification).

The use of a foam as a base structure generate new problems which are specific of its microporosity. One of the goal of the present invention is to deposit a conductive polymer on the whole surface of the openings of the structure without clogging them (page 5, line 9).

Moreover, Jolly uses a usual oxidizing agent like FeCl_3 or nitric acid (Column 3, line 32-44). The JP 6-248491 reference teaches a method of producing metallic or metallized complex porous structures comprising the steps of oxidising the materials with a solution of an oxidant, depositing in the gas phase, on the surfaces of the base structure, a monomer and polymerization by oxidation-doping of the monomer into an electroconductive polymer.

The present invention differs from the JP 6-248491 reference:

- by using a solution containing the permanganate/manganate salts and/or cerium IV compounds in the oxidising step,
- by the rinsing step subsequent to the oxidizing step,
- by depositing a monomer which in polimerized form is electrically conductive, in a wet phase,
- draining and drying following the rinsing step subsequent to the oxydizing, draining after water washing step, drying following the rinsing and draining subsequent to the polymerization by oxidation-doping; and repeating steps (2), (3), and (4) a pre-selected number of times.

According to the present invention, the oxidising pre-treatment, i.e. the first step of the process, is essential and has a double function in producing products according to the invention.

Firstly, it localizes precipitation of the monomer solely on the surface of the fibers or openings within the complex porous structure. Thus, surface priming is carried out by etching the constituent organic material, which produces a surface microporosity leading to the production of an excellent bonding surface for the latter deposit of the monomer.

Secondly, it takes part in polymerizing the monomer from the lower or hidden face deposit. This second function is equally fundamental when one considers that the metallization to be carried out following the premetallization with the conductive polymer must itself be carried out within the complex structure, through its entire thickness. The fineness of the openings, the thinness of the monomer deposit and hence of the polymer, and the limited intrinsic conductivity of the polymer obtained all necessitate a polymerization of the precipitate monomer which is as complete as possible. For this, it is necessary that oxidation of monomer should undergo oxidizing attack which leads to its polymerization not only from its outer surface, but also from its lower hidden face adhering to the bonding surface of the structure's openings of the foam. According to the description, page 9, line 9-10, it is very important that polymerization of the monomer take place from both sides. Not in the claims.

In order to obtain this two essential functions, the oxidising pretreatment is carried out by using a solution containing permanganate/manganate salts and/or cerium IV compounds, page 8, first paragraph of the description. Compared to the numerous oxidizing means such as the ferric

chloride used in JP 6-248491 and in WO94/25967 reference, the permanganate/manganate salts and/or cerium IV compounds have essential properties that are necessary to obtain the final products of the invention having all the disclosed advantages and features. For this, it is indispensable that deposition of the monomer, before its later conversion in a conductive polymer, must have taken place over the entire surface of the openings, without clogging the surface and internal porosity of the foam (page 7, line 24-27).

The use of this pre-treatment solution in the specific conditions as disclosed in the example 1, has the advantage of leading to the formation, at the surface of the openings of the foam, of a layer of oxydized products of the oxidizer such as manganese dioxide (MnO_2). These oxydized products must be insoluble and must have a sufficient oxidising power to produce the oxidation and therefore, the polymerization of the monomer by its lower face, see example 1, third paragraph. Obviously, these two properties are essential in order to obtain a good deposit of the monomer properly attached on the fibers or openings due to a polymerisation of the monomer in contact with the oxidized products on the surface of the porous structure, e.i the foam. The layer of insoluble oxidized products only appears when using permanganate/manganate salts and/or cerium IV compound as oxidizer.

Even if the applicants note that DE 4,023,619 and He et al. references mentions, among others, the possible use of permanganate and manganate salts in the oxidizing pre-treatment. Nevertheless, any references concerning methods of producing metallic or metallized complex porous structures uses those compounds in examples and all references uses ferric chloride in

their best embodiment. He et al. defines ferric chloride as the best compound (column 4, line 28) and, in column 2, line 18-26 and column 5, line 54-55, the process includes the step of coating an oxidizer in order to obtain a foam stuck with the oxidizer. None refers to the presence of insoluble oxydized products of the oxidizer having oxidizing activity on the monomer. In fact, those references disclose the direct use of the oxidizer, and not the remaining insoluble oxidizing products as defined above, coated and stuck on the foam in order to polymerize the monomer on the hidden lower face of the foam.

Consequently, as a further difference compared to the invention, the applicants note that, as mentioned above, any document refers to a rinsing step subsequent to the oxidizing step. This can easily be explained by the fact that ferric chloride deposit is soluble and, thus, a rinsing step would take the oxidizer off from the foam. Without rinsing step, the deposit of ferric chloride is obtained by *in situ* crystallization of the oxidizer, which is not properly attached to the fibers and leads to the formation of an irregular coating of the structure surface. In addition, because of the solubility of ferric chloride deposit, a depositing step of the monomer in a wet phase is impossible.

Bearing in mind all the sub-mentioned differences between the invention and the references cited by the Examiner, it is clear that the oxidizing property of permanganate/manganate salts and/or cerium IV compounds is used in order to coat the surface of the openings of the foam, of a layer of insoluble oxydized products such as manganese dioxide and not as a direct oxidizer of the monomer. Any document neither discloses nor

• suggests this essential feature. Advantageously, the presence of these oxydized products allows to easily and immediately rinse the structure after the oxidizing pre-treatment in order to avoid undesirable thinning of the structure and/or rupture of the openings of the foam (page 9, line 25-34 of the description).

In conclusion, the combination of all steps of the process allows to have a new product with a rapid and uniform deposit of polymer and, thus, of metal over the entire surface of each opening of the foams. The use of the new process according to the invention leads to obtain new products with new and inventive specific features compared to the prior art products.

Hence, a skilled person will not expect that the monomer and metal deposit and the speed of the whole metallizing process over a porous complex structure may be improved by using a solution containing permanganate/manganate salts and/or cerium IV compounds in the oxidizing pre-treatment followed by an essential rinsing step.

The JP 6-248491 reference teaches a method of producing metallic or metallized foam obtained from a polyurethane foam coated with polypyrrole. As the applicant explains above, the methods to obtain these products are very different, particularly concerning the oxidative agent used in the first step. The JP 6-248491 reference also differs from the present invention :

- by using an acetonitrile solution as an polymerisation agent

It is well known by the man skilled in the art that the acetonitrile treatment leads to an alteration of the structure of polyurethane foam. In other words, the foam swells and, consequently, leads to a possible diminution of the polypyrrole deposit homogeneity.

Moreover, referring to the JP 6-248491, the final metallized product gives the tensile strength of about 3 kgf/cm (see abstract). In the same thermal conditions and after the same Ni electrocoating to form a Ni film of 20 microns on the holes and fibers of a foam of 100 ppI Grade which were precoated with polypyrrole according the method of the present invention, the final metallized foam gives the tensile strength of about 4 kgf/cm. These results confirm the structural differences between the claimed product and the prior art products and the direct effect of the used process on the final products.

By more, the applicants note that DE 4,023,619 refers to different base structure but never to foam. On the contrary, DE 4,023,619 concerns structures which present a $100\Omega/\text{cm}$ resistance (column 2, line 28-31) which corresponds to a 500 squared surface resistance. In the present invention, the foams have a 25 squared surface resistance (page 19, line 7). As it clearly appears in the comparative test of the present application (page 20, line 3-7), these differences in the surface resistance value leads to a difference in the metal propagation speed during the metallization step. Consequently, a low propagation speed, i.e. high resistance will lead to a low metallization limited to the surface. On the contrary, a high propagation speed will lead to a good homogeneous metal deposit.

Thus, even if, according to the Examiner, the products seems to be identical because they comprise structural similarities and quite the same numbers of coatings, the microphysical and physical features of the metallized products are very different. All these elements confirms the structural differences between the claimed product and the prior art products and the direct effect of the used process on the final products.

It is noted that amended claim meet requirements of patentability and it is believed that all formal requirements are now fulfilled by the present amendment so the application should be in order to proceed to acceptance.

No additional claim fee is required by this Amendment.

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

On page 1, line 2 add

Cross-Reference to Related Applications

This application is a Divisional of U.S. Patent Application Serial No. 08/691,241 filed August 2, 1996, now U.S. Patent No. 6,290,832, the disclosure of which is being incorporated herein by reference in its entirety.

Abstract

The invention concerns the manufacture of complex metallic or metallized porous structures, wherein the electroplating metal over the entire developed surface is preceded by a specific pre-metallization of the basic structure. The pre-metallization is obtained by depositing a conductive polymer, which is deposited on the entire developed surface of the structure by the steps of an oxidizing pre-treatment of the structure, depositing in the liquid phase, a monomer having a polymerized [foam] form that is electrically conductive, and polymerizing by oxidation-doping of the monomer. The structures according to the invention are particularly intended for use as electrodes for the electrolysis of liquid effluents, as electrode supports for electrochemical generators, as catalyst supports, filtration media, phonic insulation, electromagnetic and nuclear protection structures, or for other applications.

Claims:

Claim 14. (Twice Amended) A complex porous structure of reticulated material produced by a process comprising :

electroplating said material with metal substantially throughout its entire thickness, over all its developed surface, subsequent to [pre-metalization] pre-metallizing,

[said pre-metallization] pre-metallizing comprising depositing a conductive polymer on the surface of the fibers or the opening of the structure, said depositing comprising :

(1) oxidising a base structure comprising pores, consisting of a reticulated cellular structure of high porosity greater than 80%, with a solution containing permanganate/manganate salts and/or cerium IV compounds;

(2) rinsing and drying,

(3) depositing, in a wet phase, on surfaces of the base structure, a monomer which in polymerized form is electrically conductive;

(4) polymerisation [of the monomer] by oxidation-doping of the monomer into an electrically conductive polymer; and

(5) rinsing, wherein said steps are carried out on the base structure, substantially throughout its entire thickness, without clogging the pores of the base structure.

Claim 18. (Amended) The structure according to claim 14, wherein the monomer deposited is selected from the group consisting of pyrrole[, and polypyrrole].

Claim 22. (Amended) A metallized structure [produced by electroplating the complex porous structure] produced by claim 14 wherein said electroplating is carried out in an electrolysis bath comprising ions which stabilize or oxidize an anodic structure.

Claim 25. (Amended) The metallized structure according to claim 22, wherein said metal used for electroplating is selected from the group consisting of copper, nickel, iron, chromium, zinc, aluminum, tin, lead, gold, platinum, and an alloy mixture of at least two of said metals[, and superposition of at least two of said metals].

Claim 27. (Amended) The complex porous structure of claim 26, comprising draining following the rinsing subsequent to the polymerization [of] by oxidation-doping of the monomer.

Claim 28. (Amended) The complex porous structure of claim 27, comprising drying following the draining following the rinsing subsequent to the polymerization [of] by oxidation-doping of the monomer.

Claim 29. (Amended) The complex porous structure of claim 28, comprising draining following the rinsing subsequent to the oxidizing pre-treatment of the base structure.

Claim 30. (Amended) The complex porous structure of claim 29, comprising repeating said steps following the rinsing subsequent to the oxidizing pre-treatment of the base structure a preselected number of times.